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Synthesis of ruthenium(II) complexes derived from reduced imine ligands: As catalysts for transfer hydrogenation of ketones

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ABSTRACT

N-[2-(benzylamino)phenyl]benzenesulfonamide derivatives (**1**–**6**) were successfully synthesized by the reaction of imine ligands derived from various *N*-(2-aminophenyl)benzenesulfonamides and $NaBH_4$. Then, a series of *N*-coordinate Ru(II) arene complexes **7**–**12** were prepared from the reaction of $[RuCl_2(p\text{-}cymene)]_2$ with **1**–**6**. The synthesized compounds were characterized by different methods such as NMR, FT-IR, and elemental analysis. **7**–**12** were used as catalysts for the transfer hydrogenation (TH) of ketones. At the same time, the effect of various bases such as NaOH, KOH, $KOBu^t$ and Et_3N as organic base were investigated in TH of ketones by 2-propanol as the hydrogen source. **7**–**12** showed good catalytic activity and so the effects of the different groups were also examined.

1. Introduction

In general, sulfonamides are obtained from the reaction of sulfonyl chloride with primary or secondary amines in alkaline [1]. The sulfonamides and their derivatives have attracted the interest of many researchers due to their importance in the development of coordination chemistry, their application in medicinal chemistry, catalytic fields, etc. [2–18]. For example, metal complexes containing sulfonamide ligands have been used as catalysts in different organic reactions [19–26].

The transfer hydrogenation (TH) of ketones catalyzed by Ru(II) complexes bearing *N*-donor ligands has been attracting more and more attention from the catalysis community [27–38] since the success of Noyori's catalyst, bearing 1,2-diamine ligands [39]. After Noyori et al., researchers, many derivatives of Ru(II) complexes containing *N*-donor ligands have aimed to identify a good Ru(II) catalyst for the TH of ketones. Hereof, ligand groups which have Ru(II) complexes with unique catalytic activity are sulfonamides.

Otherwise, Schiff base and reduced Schiff base compounds are also receiving more and more attention in the fields of polymeric complexes, coordination chemistry, magnetic properties, optical property, thermal decomposition, medicinal chemistry, catalyst chemistry, etc. [40–69]. In addition, palladium complexes bearing diamine and diimine were used as catalyst for Suzuki Cross-Coupling [70]. Further, the TH of acetophenone was carried out by ruthenium(II) complexes of reduced Schiff base ligands. The Ru(II) complexes were found as active catalyst [71]. *N*-heterocyclic carbene (NHC) ligands derivatives from reduced Schiff base ligands have been synthesized. Then, a series of Ru(II) complexes were prepared with the NHC ligands. The complexes were used for the catalytic transfer hydrogenation of aromatic ketones, recently [72].

In this place, a series of neutral Ru(II) arene complexes derived from reduced imine ligands bearing aromatic sulfonamide were synthesized and characterized by various spectroscopic techniques. **7**–**12** were used as catalysts for the TH of *p*-substituent acetophenone derivative. The synthesis procedure of ligands **1**–**6** and complexes **7**–**12** are simple and does not require an inert atmosphere and it can be carried out in at mild-temperatures.

2. Experimental

2.1. Materials and methods

All reagents and solvents were obtained from commercial suppliers and used without any additional purification. NMR spectra were recorded at 297 K on a Bruker 400 NMR spectrometer at 400 MHz (^1H) and 100.56 MHz (^{13}C). The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J*-values) are given in hertz. NMR multiplicities are abbreviated as follows: br = broad, s =

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singlet, d = doublet, t = triplet, m = multiplet signal. The C, H, and N analyses were performed using a Truspec MICRO (LECO) instrument. Infrared spectra were measured with a Perkin-Elmer Spectrum 400 FTIR system and recorded using a universal ATR sampling accessory within the range 550–4000 cm^{-1}. Melting points were determined in open capillary tubes on a digital Electrothermal 9100 melting point apparatus. GC measurements for catalytic experiments were performed using a Younglin Acme 6100 GC instrument with a flame ionization detector and an Optima 5MS capillary column (The GC parameters were as follows: oven: 80 °C (isothermal); Carrier gas: H_2 (Split ratio 15:1); Flow rate: 4 mL/min; injector port temperature: 220 °C; Detector temperature: 280 °C; Injection volume: 6.0 μL).

2.2. General procedure for the synthesis of 1–6

N-(2-aminophenyl)benzenesulfonamides and the Schiff base derivatives of those compounds were prepared in accordance with the published procedure [73a–c]. Solid sodium borohydride (0.2 mmol) was added slowly to a solution of *N*-[2-(benzylamino)phenyl]benzenesulfonamide derivatives (0.2 mmol) in methanol (10 ml). The solution was stirred at ambient temperature for a period of 12 h. The volatiles were removed under reduced pressure. The residue was dissolved in DCM (20 ml) and washed with H_2O (3 × 50 ml) at room temperature. The organic layer was separated and dried over anhydrous $MgSO_4$, filtered, and concentrated to half of its volume under reduced pressure. The solution was saturated with diethyl ether and left in the refrigerator for crystallization. Gradually, a microcrystalline product separated, which was filtered off, and dried *in vacuo* (Fig. 1).

2.2.1. Data for the 1–6

(**1**)-*N*-*[2-(benzylamino)-phenyl]benzenesulfonamide*

Color: light pink. Yield: 92%. Mp: 132–133 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 4.30 (s, 2H, –C*H*$_2$–), 6.36 (br. –N*H*–), 6.47–7.35 (9H, –*H*$_{1-4}$, –*H*$_{x-z}$), 7.46 (t, 2H, *J* = 8 Hz, –*H*$_b$), 7.59 (t, 2H, *J* = 8 Hz, –*H*$_c$), 7.78 (d, 2H, *J* = 8 Hz, –*H*$_a$). ^{13}C NMR ($CDCl_3$, ppm): 48.1 (–CH_2–), 112.8 (Ar. –*C*), 117.3 (Ar. –*C*), 120.6 (Ar. –*C*), 127.3 (Ar. –*C*), 127.4 (Ar. –*C*), 127.6 (Ar. –*C*), 128.6 (Ar. –*C*), 128.7 (Ar. –*C*), 129.0 (Ar. –*C*), 129.4 (Ar. –*C*), 133.1 (Ar. –*C*), 138.5 (Ar. –*C*), 139.0 (Ar. –*C*), 145.2 (Ar. –*C*). IR (cm^{-1}): 3426 (–N*H*–CH_2–), 3255 (–N*H*), 3055, 3027, 2988, 2969, 2902, 1602, 1585, 1515, 1494, 1469, 1453, 1447, 1436, 1394, 1366 (–SO_2), 1322, 1298, 1280, 1262, 1208, 1178, 1151 (SO_2), 1122, 1088, 1060, 1049, 1026, 996, 974, 941, 909, 880, 858, 834, 804, 779, 750, 736, 727, 712, 697, 685, 665, 635, 590, 564, 539, 500, 485, 458. *Anal.* Calc. for: C: 67.43, H: 5.36, N: 8.28, O: 9.46, S: 9.47. Found: C: 67.25, H: 5.16, N: 8.35, S: 9.60%.

(**2**)-*N*-*[2-(benzylamino)-4-methoxy-phenyl]benzenesulfonamide*

Color: light pink. Yield: 84%. Mp: 119–120 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 3.83 (s, 3H, –OC*H*$_3$), 4.24 (s, 2H, –C*H*$_2$–) 6.33–7.80 (15H, –N*H*– *H*$_{1-4}$, –*H*$_{a-c}$ and –*H*$_{x-y}$). ^{13}C NMR ($CDCl_3$, ppm): 47.26 (–CH_2–), 55.2 (–OCH_3), 112.3 (Ar. –*C*), 114.0 (Ar. –*C*), 116.7 (Ar. –*C*), 120.2 (Ar. –*C*), 127.5 (Ar. –*C*), 126.6 (Ar. –*C*), 128.5 (Ar. –*C*), 128.7 (Ar. –*C*), 128.9 (Ar. –*C*), 129.3 (Ar. –*C*), 130.7 (Ar. –*C*), 133.0 (Ar. –*C*), 138.9 (Ar. –*C*), 145.6 (Ar. –*C*). IR (cm^{-1}): 3434 (–N*H*–CH_2–), 3242 (–N*H*), 3002, 2909, 2837, 1603, 1583, 1510, 1467, 1445, 1401, 1365 (–SO_2), 1323, 1286, 1245, 1207, 1178, 1150 (–SO_2), 1092, 1071, 1047, 1029, 992, 989, 913, 832, 807, 753, 740, 730, 711, 686, 632, 595, 558, 535, 462. *Anal.* Calc. for: C: 65.20, H: 5.47, N: 7.60, O: 13.03, S: 8.70. Found: C: 65.12, H: 5.60, N:7.52, S:8.63%.

(**3**)-*N*-*[2-(benzylamino)-4-methyl-phenyl]benzenesulfonamide*

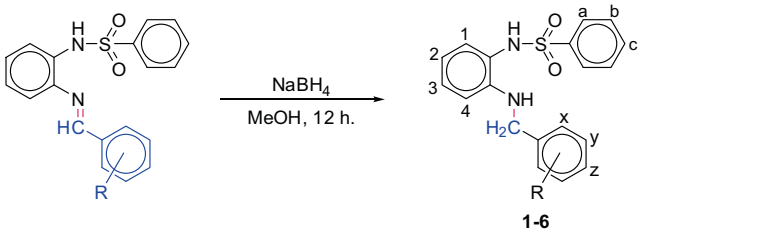
Color: light pink. Yield: 80%. Mp: 162–163 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 2.35 (s, 3H, –C*H*$_3$), 4.25 (s, 2H, –C*H*$_2$–), 6.54–7.80 (15H, –N*H*–, *H*$_{1-4}$, –*H*$_{a-c}$, and –*H*$_{x-y}$). ^{13}C NMR ($CDCl_3$, ppm): 21.1 (–CH_3), 48.22 (–CH_2–), 118.0 (Ar. –*C*), 127.3 (Ar. –*C*), 127.6 (Ar. –*C*), 128.5 (Ar. –*C*), 129.0 (Ar. –*C*), 129.2 (Ar. –*C*), 129.3 (Ar. –*C*), 129.8 (Ar. –*C*), 130.0 (Ar. –*C*), 131.9 (Ar. –*C*), 132.7 (Ar. –*C*), 133.1 (Ar. –*C*). IR (cm^{-1}): 3441 (–N*H*–CH_2–), 3205 (–N*H*), 3073, 3045, 3017, 2932, 2916, 2856, 2783, 1600, 1581, 1514, 1482, 1467, 1448, 1436, 1406, 1362 (–SO_2), 1326, 1317, 1300, 1282, 1252, 1205, 1179, 1162 (–SO_2), 1146, 1128, 1113, 1091, 1072, 1048, 1020, 999, 992, 940, 920, 833, 797, 779, 758, 747, 730, 711, 665, 668, 647, 639, 596, 561, 533, 517, 506, 474. *Anal.* Calc. for: C: 68.16, H: 5.72, N: 7.95, O: 9.08, S: 9.10. Found: C: 68.22, H: 5.62, N: 7.99, S: 9.02%.

(**4**)-*N*-*[2-(benzylamino)-2,4-di-methyl-phenyl]benzenesulfonamide*

Color: dark orange. Yield: 78%. Mp: 110–111 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 2.32 (s, 3H, –(CH_3)$_p$), 2.34 (s, 3H, –(CH_3)$_o$), 4.19 (s, 2H, –C*H*$_2$–), 4.75 and 6.08 (br. 2H, –N*H*–), 6.46–7.78 (12H, *H*$_{1-4}$, –*H*$_{a-c}$, and –*H*$_{x-y}$). ^{13}C NMR ($CDCl_3$, ppm): 18.9 (–(CH_3)$_p$), 21.0 (–(CH_3)$_o$), 45.7 (–CH_2–), 112.0 (Ar. –*C*), 116.6 (Ar. –*C*), 120.1 (Ar. –*C*), 126.8 (Ar. –*C*), 127.6 (Ar. –*C*), 128.0 (Ar. –*C*), 128.7 (Ar. –*C*), 129.0 (Ar. –*C*), 129.5 (Ar. –*C*), 131.3 (Ar. –*C*), 133.1 (Ar. –*C*), 133.4 (Ar. –*C*), 136.0 (Ar. –*C*), 136.9 (Ar. –*C*), 139.0 (Ar. –*C*), 145.9 (Ar. –*C*). IR (cm^{-1}): 3431 (–N*H*–CH_2–), 3273 (–N*H*), 3064, 3001, 2972, 2919, 2866, 1606, 1584, 1520, 1506, 1470, 1448, 1395, 1361 (–SO_2), 1326, 1285, 1272, 1248, 1231, 1207, 1179, 1157 (–SO_2), 1093, 1070, 1048, 1027, 1000, 980, 932, 925, 906, 873, 852, 827, 813, 784, 757, 739, 729, 712, 686, 638, 597, 565, 553, 536, 489, 462. *Anal.* Calc. for: C: 68.82, H: 6.05, N: 7.64, O: 8.73, S: 8.75. Found: C: 68.90, H: 6.12, N: 7.60, S: 8.66%.

(**5**)-*N*-*[2-(benzylamino)-2,4,6-tri-methyl-phenyl]benzenesulfonamide*

Color: white. Yield: 86%. Mp: 152–153 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 2.32 (s, 3H, –(CH_3)$_p$), 2.33 (s, 6H, –(CH_3)$_o$), 4.15 (s, 2H, –C*H*$_2$–), 6.03–7.75 (13H, –N*H*–, *H*$_{1-4}$, –*H*$_{a-c}$, and –*H*$_y$). ^{13}C NMR ($CDCl_3$, ppm): 19.4 (–(CH_3)$_o$), 21.0 (–(CH_3)$_p$), 42.2 (–CH_2–), 111.9 (Ar. –*C*), 116.6 (Ar. –*C*), 120.3 (Ar. –*C*), 127.5 (Ar. –*C*), 128.5 (Ar. –*C*), 128.9 (Ar. –*C*), 129.1 (Ar. –*C*), 129.4 (Ar. –*C*), 131.4 (Ar. –*C*), 133.0 (Ar. –*C*), 137.3 (Ar. –*C*), 137.5 (Ar. –*C*), 139.0 (Ar. –*C*), 145.9 (Ar. –*C*). IR (cm^{-1}): 3413 (–N*H*–CH_2–), 3307 (–N*H*), 3073, 2964, 2923, 2872, 1601, 1584, 1509, 1475, 1447, 1377 (–SO_2), 1333, 1320, 1310, 1290, 1274, 1250, 1221, 1208, 1181, 1162 (–SO_2), 1121, 1089, 1073, 1063, 1048, 1022, 996, 933, 888, 854, 845, 826, 753, 728, 717, 691, 672, 632, 596, 570, 543, 500, 471. *Anal.* Calc. for: C: 69.44, H: 6,36, N: 7.36, O: 8.41, S: 8.43. Found: C: 69.54, H: 6,42, N:7.25, S:8.33%.



R= -C_6H_5 :(1) -*p*-methoxy-Ph :(2) -*p*-methyl-Ph: (3) -$C_6H_3Me_2$-2,4: (4) -$C_6H_2Me_3$-2,4,6: (5) -*p*-chloro-Ph: (6)

Fig. 1. Synthesis of the ligands together with NMR numbering scheme.